Effects of surfactant addition to draw solution on the performance of osmotic membrane bioreactor

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Abstract

This study investigated the effects of surfactant addition to the draw solution on the performance of osmotic membrane bioreactor (OMBR). Forward osmosis (FO) tests were conducted with the addition of sodium dodecyl benzene sulfonate (SDBS), a representative surfactant, to both inorganic and ionic organic draw solutions, including sodium chloride (NaCl), sodium acetate (NaOAc), and sodium propionate (NaPro), to determine the desirable draw solution for OMBR operation. Results show that SDBS impacts were more notable for inorganic draw solution in comparison to its ionic organic counterparts at the same osmotic pressure (60 bar) in FO operation. In specific, SDBS addition up to 5 mM considerably reduced the reverse diffusion of NaCl draw solute (approximately 69.7%) with insignificant impact on water flux. Thus, salinity build-up in the bioreactor could be effectively mitigated when SDBS was added to the NaCl draw solution in OMBR operation. This mitigation led to stable sludge characteristics and biological treatment to sustain OMBR performance regarding water production (approximately 10 L/m^2h) and contaminant removal (over 90% for pharmaceutically active compounds).

Keywords: Osmotic membrane bioreactor; Forward osmosis; Salinity build-up; Sodium dodecyl benzene sulfonate; Wastewater treatment

1. Introduction

Safe and adequate access to clean water remains a pervasive challenge to our sustainable development. It has been speculated that over three billion people would live under water-scarce and water-stressed conditions by 2025 [1]. More alarmingly, water scarcity is deteriorated by global climate change, population growth, and environmental pollution, which easily occur in developing and industrialized countries [2]. Wastewater treatment and reuse is a pragmatic strategy to simultaneously address water scarcity and environmental problems [3]. Nevertheless, the current wastewater treatment facilities are challenged by strict water regulations and ubiquitous occurrence of trace organic contaminants (TrOCs), such as pharmaceutically active compounds (PhACs), personal care products, and endocrine disruptor [4]. In particular, PhACs have become the main TrOCs of emerging concern due to overuse of pharmaceuticals, such as antibiotics and analgesic substances [5].

Membrane bioreactor (MBR), which combines conventional biological treatment and membrane separation process, has been globally deployed for wastewater treatment and water reclamation. By using porous membrane processes, such as microfiltration and ultrafiltration, MBR enables the effective removal of emerging contaminants from wastewater. For instance, it has been widely reported that MBR could effectively remove several emerging TrOCs, particularly those easily biodegradable and/or hydrophobic compounds, such as estrone, bisphenol A, and salicylic acid [6, 7]. Nevertheless, some hydrophilic and biologically persistent contaminants, such as PhACs, are recalcitrant to MBR treatment (less than 30%) and require further elimination, for example, by reverse osmosis (RO), advanced oxidation, and adsorption [8, 9].

Recent progress in MBR has led to the development of osmotic membrane bioreactor (OMBR) to advance wastewater treatment and reuse [10-12]. OMBR integrates forward osmosis (FO), an osmotically driven membrane process, with the biological treatment. Previous studies have well evidenced the superiority of OMBR over conventional MBR in wastewater treatment and reuse, particularly in terms of product

water quality, energy consumption, and membrane fouling propensity and reversibility [13, 14]. For example, Luo et al. [15] demonstrated that OMBR could improve the removal of 31 TrOCs in comparison with conventional MBR, and thus relieving the treatment stress on downstream RO unit.

Although OMBR holds promise to advance wastewater treatment and reuse, its further development is hindered by salinity build-up within the bioreactor [9]. Salinity build-up is an intrinsic issue to OMBR due to the effective FO retention of inorganic salts from wastewater and reverse solute flux from draw solution. Ample evidences have clearly demonstrated that salinity build-up could detrimentally impact OMBR performance by disturbing biological stability, reducing effective driving force, and aggravating membrane fouling [16, 17]. Thus, several strategies have been developed to address salinity build-up for sustainable OMBR operation. These mainly include developing high selective FO membrane [10], enhancing sludge discharge [18], integrating with porous membrane for salt release [9], and employing suitable draw solution [8].

Draw solution in OMBR can significantly affect water flux and salinity build-up in the bioreactor. Inorganic draw solutions, such as sodium chloride (NaCl) and magnesium chloride, have been widely used for OMBR due to their effective osmotic pressure and diffusivity to induce high water flux [9]. Nevertheless, high reverse diffusion of inorganic draw solutes results in severe salinity increase in the bioreactor and thus deteriorates OMBR performance [9]. Recent studies have suggested that surfactants could reduce the reverse diffusion of inorganic draw solutes. For instance, Nguyen et al. [19] observed a sustainable water flux and low salt accumulation in the bioreactor when a sponge-based moving bed OMBR was continuously operated for 90 days with the addition of polyethylene glycol tert-octylphenyl ether (Triton X-114) to the $MgCl_2$ draw solution. Furthermore, Wang et al. [20] demonstrated the outperformance of sodium dodecyl benzene sulfonate (SDBS) out of six different surfactants to mitigate the reverse flux of NaCl draw solute in FO operation. Nevertheless, the role of SDBS in OMBR operation and performance remains unknown.

Ionic organic draw solutions have been proposed to mitigate salinity build-up in the bioreactor during OMBR operation. Compared to their inorganic counterparts, ionic organic draw solutes could contribute comparable water flux, but much lower reverse solute flux due to their relatively large molecular weight, and thus smaller diffusivity [21]. Moreover, organic components reversed from the ionic organic draw solutions could be biodegraded by activated sludge [9]. Nevertheless, severe membrane fouling may occur due to reverse organic diffusion to provide carbon source for biofilm development on the membrane surface. For instance, Luo et al. [8] demonstrated that sodium acetate (NaOAc) as the draw solution could effectively control salinity build-up in the bioreactor, but still resulted in notable flux decline with cohesive and thick fouling layer on the FO membrane surface in OMBR operation. Thus, strategies to further mitigate the reverse diffusion of ionic organic draw solutes need to be developed to sustain OMBR operation.

Inspired by recent studies, this study aims to evaluate the effects of surfactant addition in the draw solution on OMBR performance. SDBS highlighted in recent studies was used as the representative surfactant [20]. FO tests were conducted to compare SDBS impacts on the water flux and reverse diffusion of both inorganic and ionic organic draw solutes to determine the draw solution for OMBR operation. OMBR performance was assessed with respects to water production, sludge characteristics, and PhAC removal. Results from this study will provide important insights to manage salinity build-up in the bioreactor for practical OMBR applications.

2. Materials and methods

2.1 Synthetic wastewater and pharmaceutically active compounds

Synthetic wastewater, simulating medium strength municipal sewage, was used as the OMBR influent. The synthetic wastewater was formulated daily and comprised 100 mg/L glucose,100 mg/L peptone, 17.5 mg/L KH_2PO_4, 17.5 mg/L $MgSO_4$, 10 mg/L $FeSO_4$, 10 mg/L $CuSO_4$, 10 mg/L $ZnSO_4$, 10 mg/L $MnCl_2$, 225 mg/L CH_3COONa, and 35 mg/L urea. Basic physiochemical properties of the synthetic wastewater were

measured every three days and mainly contained 133.18 ± 9.99 mg/L total organic carbon (TOC), 33.50 ± 4.09 mg/L total nitrogen (TN), 1.40 ± 0.80 mg/L ammonium nitrogen (NH_4^+-N), 3.51 ± 0.63 mg/L total phosphorus (TP). Moreover, the electrical conductivity (EC) and pH of the synthetic wastewater were 242.00 ± 9.78 μS/cm and 5.60 ± 1.01, respectively.

A set of 12 PhACs that ubiquitously present in wastewater and sewage-impacted water bodies were introduced to the synthetic wastewater. These compounds can be categorized into four groups, including sulfonamides, tetracyclines, fluoroquinolones, and macrolides. A stock solution containing 50 μg/mL of each compound was prepared in pure methanol and stored at –20 °C in the dark. The stock solution was added into the synthetic wastewater to obtain a concentration of 5 μg/L of each compound. Key physiochemical properties of the 12 compounds are shown in Table S1, Supplementary Data.

2.2 Draw solutes and FO membrane

Performance of NaCl, NaOAc, and NaPro draw solutes was compared in this study. NaCl is a widely used draw solute due to its high osmotic pressure, low cost, and stable physiochemical properties. NaOAc and NaPro are ionic organic draw solutes and can produce comparable water flux, but much less reverse solute flux than NaCl during FO operation [22, 23]. SDBS was used to modify these draw solutes to reduce their reverse solute fluxes [20]. All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd.

A flat-sheet, thin-film composite FO membrane obtained from Aquaporin Asia (Aquaporin A/S, Singapore) was used. The FO membrane consisted of a polyamide selective layer with the embedment of aquaporin protein vesicles and a porous polysulfone supporting layer [10]. Key physiochemical characteristics of the aquaporin FO membrane have been demonstrated in our previous studies [10, 24]. Briefly, the FO membrane had a water permeability of 2.09 ± 0.02 L/m^{2}h-bar, solute permeability of 0.07 ± 0.01 L/m^{2}h, structural parameter of 301 ± 36 μm [24], and estimated pore radius

of 0.30 nm [25].

2.3 Experimental systems and protocols

This study included two experimental sections using FO and OMBR systems, respectively. The FO system was used to screen the draw solution and determine the appropriate surfactant concentration for OMBR operation. Subsequently, the OMBR system was then used to validate the results from FO tests by evaluating surfactant performance to control salinity build-up in the bioreactor.

2.3.1 FO evaluation

A bench-scale, closed-loop FO system consisting of a cross-flow membrane module and two variable speed gear pumps was employed (Fig. S1A, Supplementary Data). Details of the FO system are available elsewhere [26]. Briefly, the membrane module was made of acrylic plastic and had two identical flow chambers with a length, width, and height of 100, 50, and 2 mm, respectively. The FO membrane was sealed between two flow chambers with an effective membrane area of 50 cm^2. The two variable speed gear pumps (Micropump, Vancouver, WA) were used to circulate feed and draw solutions at a cross-flow velocity of 8.3 cm/s. The draw solution reservoir was placed on a digital balance (Mettler Toledo, Hightstown, NJ) connected to a computer to record the weight change for water flux calculation.

The FO system was operated in the osmotic dilution mode in a temperature-controlled room (25 ± 1 ^oC). Three draw solutions were evaluated individually at the initial osmotic pressure of 60 bar. Based on the simulation results from the OLI Stream Analyzer software (OLI Systems, Morris Plains, NJ), the three draw solutions were 1.2 M NaCl, 1.5 M NaOAc, and 1.6 M NaPro, respectively. SDBS was added to these draw solutions at different concentrations (in the range of 0 – 7 mM). Deionized water was used as the feed solution to contact the membrane active layer. The initial volume of both feed and draw solutions was 1 L. All FO tests were conducted for 2 h after the membrane was stabilized for 1 h.

Feed solution EC was measured every 0.5 h to calculate the reverse solute flux based

183 on the concentration-EC standard curve of each draw solute [23, 27]. Since SDBS
184 surfactant hardly transported through the FO membrane [20], EC increase in feed
185 solution was caused by reverse draw solute. All tests were performed in duplicate using
186 new membrane coupons.

187 *2.3.2 OMBR operation*

188 Two identical bench-scale, submerged OMBR systems were used (Fig. S1B,
189 Supplementary Data). Each system mainly comprised a wastewater reservoir, an
190 aerobic bioreactor, a plate-and-frame FO membrane module, a draw solution reservoir,
191 and a control unit. A level controller was used to feed wastewater into the bioreactor to
192 maintain the reactor working volume of 8 L. The FO membrane module was made of
193 acrylic plastic with a draw solution flow chamber of 150 mm length, 80 mm width, and
194 3 mm height. The FO membrane was sealed on the flow chamber with the active layer
195 (effective area of 120 cm^2) in contact with the mixed liquor. A gear pump was utilized
196 to circulate the draw solution to the membrane module at a cross-flow velocity of 8.3
197 cm/s. The draw solution reservoir was placed on a digital balance to record weight
198 increase to calculate water flux.

199 Activated sludge obtained from a local Wastewater Treatment Plant (Beijing, China)
200 was used to inoculate the bioreactor. The activated sludge was acclimatized to the
201 synthetic wastewater for more than two months in conventional MBR. After the MBR
202 achieved stable performance as indicated by over 95% TOC removal, the sludge
203 concentration in the bioreactor was adjusted to approximately 5 g/L and then
204 transformed to the OMBR system.

205 The two OMBR systems were operated and compared in parallel using the draw
206 solution determined from FO evaluation above with and without SDBS addition,
207 respectively. The bioreactors were continuously aerated to maintain dissolved oxygen
208 concentration of approximately 4 mg/L. Mixed liquor was daily discharged (400 mL)
209 to keep the sludge retention time (SRT) of 20 days. The operating hydraulic retention
210 time (HRT) was determined by the FO water flux. Draw solution in each OMBR system

had a working volume of 1.5 L and was refreshed every 12 hours to maintain osmotic pressure for water permeation and minimize contaminant accumulation. In practice, an additional desalination technique, such as RO and membrane distillation (MD), can be potentially integrated with OMBR for draw solution regeneration and clean water production [15, 28]. It is noteworthy that MD can be potentially used to treat wastewater containing high concentrations of surfactants with the rapid development of superhydrophobic and omniphobic membranes [29, 30]. The OMBR experiment was continuously operated for 21 days without any membrane cleaning in the same temperature-controlled room as FO tests. Aqueous samples were collected from wastewater, mixed liquor supernatant, and draw solution every three days to analyze their basic water parameters. Mixed liquor was taken every four days for biomass characterization. Notably, all samples were collected when the diluted draw solution was renewed.

2.4 Analytical methods

2.4.1 Water flux and reverse solute flux

Water flux (J_w, L/m^{2}h) was determined as:

$$J_w = \frac{\Delta V}{A\Delta t} \quad (1)$$

where ΔV was the increased volume of draw solution (L) over a certain period, Δt (h); and A was the effective membrane area (m^2).

Reverse solute flux (J_s, g/m^{2}h) of the draw solution was determined as:

$$J_s = \frac{V_t C_t - V_0 C_0}{At} \quad (2)$$

where V_0 and V_t were feed solution volumes at the beginning and a certain time (t) in FO operation, respectively; C_0 and C_t were feed solution concentrations at the beginning and a certain time (t) in FO operation, respectively.

2.4.2 Basic water quality parameters

TOC and TN were measured using a TOC/TN analyzer (TOC-V_{CSH}, Shimadzu, Kyoto).

237 NH_4^+-N was determined by a Flow Injection Analyzer (QuikChem 8500, Lachat, CO).
238 The ammonium molybdate spectrophotometric method was used to quantify TP.
239 Solution pH and EC were monitored using an Orion 4-Star Plus pH/conductivity meter
240 (Thermo Scientific, Waltham, MA). Since contaminants passed through the FO
241 membrane could be diluted by draw solution during OMBR operation, a dilution factor
242 (*DF*) was used to calculate their actual concentrations in permeate as follows:

243 $$DF = \frac{V_{DS}}{V_{FO}} \quad (3)$$

244 where V_{DS} was the draw solution volume when aqueous samples were collected; and
245 V_{FO} was water volume that permeated through the FO membrane. Thus, contaminant
246 removal by OMBR (R_{OMBR}) was defined as:

247 $$R_{OMBR} = \left(1 - \frac{C_{Draw}}{C_{Feed}} DF\right) \times 100\% \quad (4)$$

248 where C_{Feed} and C_{Draw} were the measured contaminant concentrations in the feed and
249 draw solution, respectively.

250 *2.4.3 Analysis of pharmaceutically active compounds*

251 PhAC concentrations in wastewater, mixed liquor supernatant, and draw solution were
252 determined weekly based on a method described previously by Liu et al. [31]. Briefly,
253 this method included solid phase extraction, derivatization, and quantification by an
254 ultrahigh performance liquid chromatography-tandem mass spectrometry (UPLC-
255 MS/MS, Waters, Milford, MA). The mixed liquor was centrifuged at 4000 rpm for 20
256 min to obtain the supernatant.

257 PhAC removal by OMBR was calculated based on Eqs. (3) and (4). It is noted that
258 contaminant removal in OMBR was mainly contributed by biological treatment (i.e.
259 biodegradation, biotransformation and biosorption) and FO membrane rejection. PhAC
260 removal by biological treatment (R_{Bio}) was defined as follows:

261 $$R_{Bio} = \left(1 - \frac{C_{Sup}V_{Bio} + C_{Draw}DF\Delta V_{FO}}{C_{Feed}\Delta V}\right) \times 100\% \quad (5)$$

262 where C_{Sup} was the measured PhAC concentrations in the mixed liquor supernatant;

263 V_{Bio} was the effective bioreactor volume (8 L); and ΔV_{FO} was water volume that
264 permeated through the FO membrane over a certain period (Δt), which was equal to the
265 volume of wastewater fed into the bioreactor (ΔV).

266 According to Eqs. (4) and (5), the observed FO rejection of PhACs by the FO membrane
267 (R_{FO}) was calculated as follows:

268 $$R_{FO} = R_{OMBR} - R_{Bio} \quad (6)$$

269 It is noted that the observed rejection rates were not the actual rejection capacity of the
270 FO membrane, but its contribution to contaminant removal in OMBR.

271 *2.4.4 Biomass characteristics*

272 MLSS and mixed liquor volatile suspended solid (MLVSS) concentrations in the
273 bioreactor were determined by the Standard Method 2540 [32]. Specific oxygen uptake
274 rate (SOUR) of activated sludge that was used to indicate biomass activity was
275 measured following the Standard Method 1683 [32]. Extracellular polymeric substance
276 (EPS) in sludge was extracted using a thermal method described by Zhang et al. [33].
277 EPS extract was obtained by blending samples with 0.9% sodium chloride solution and
278 then heating at 80 ºC for 1 h. EPS and soluble microbial products (SMP) in the mixed
279 liquor were measured by quantifying their protein and polysaccharide concentrations.
280 The Folin method with bovine serum albumin as the standard [34] and the phenol-
281 sulfuric acid method with glucose as the standard [35] were used to measure the protein
282 and polysaccharide concentrations, respectively.

283 **3. Results and discussion**

284 *3.1 Effects of SDBS addition on FO performance with different draw solutes*

285 *3.1.1 Water flux*

286 Regardless of different SDBS concentrations, the NaCl draw solution produced a higher
287 water flux than both NaOAc and NaPro during FO operation (Fig. 1). Indeed, the higher
288 water flux contributed by NaCl draw solution over its ionic organic counterparts has
289 been reported previously and could be attributed to their smaller diffusion coefficients

to induce more severe internal concentration polarization (ICP) in FO operation [22, 23]. Since the SDBS concentration in the NaCl draw solution increased from 0 to 7 mM, the water flux decreased and then gradually stabilized. The decreased water flux was possibly due to the increased viscosity of draw solution with SDBS addition to aggravate ICP and thus reduce the effective osmotic pressure across the membrane for water permeation. It has been reported that SDBS could form micelles when its concentration was above the critical micelle concentration (CMC) (i.e. 2.76 mM) [20]. On the other hand, SDBS has both hydrophobic and hydrophilic functional groups, which could absorb onto the FO membrane surface through hydrophobic interaction to reduce surface tension and increase membrane hydrophilicity to enhance water permeability [36-38]. Thus, the stable water flux observed for NaCl draw solution with SDBS concentration above 5 mM could be related to the enhanced water permeation to compromise flux decline caused by increased solution viscosity.

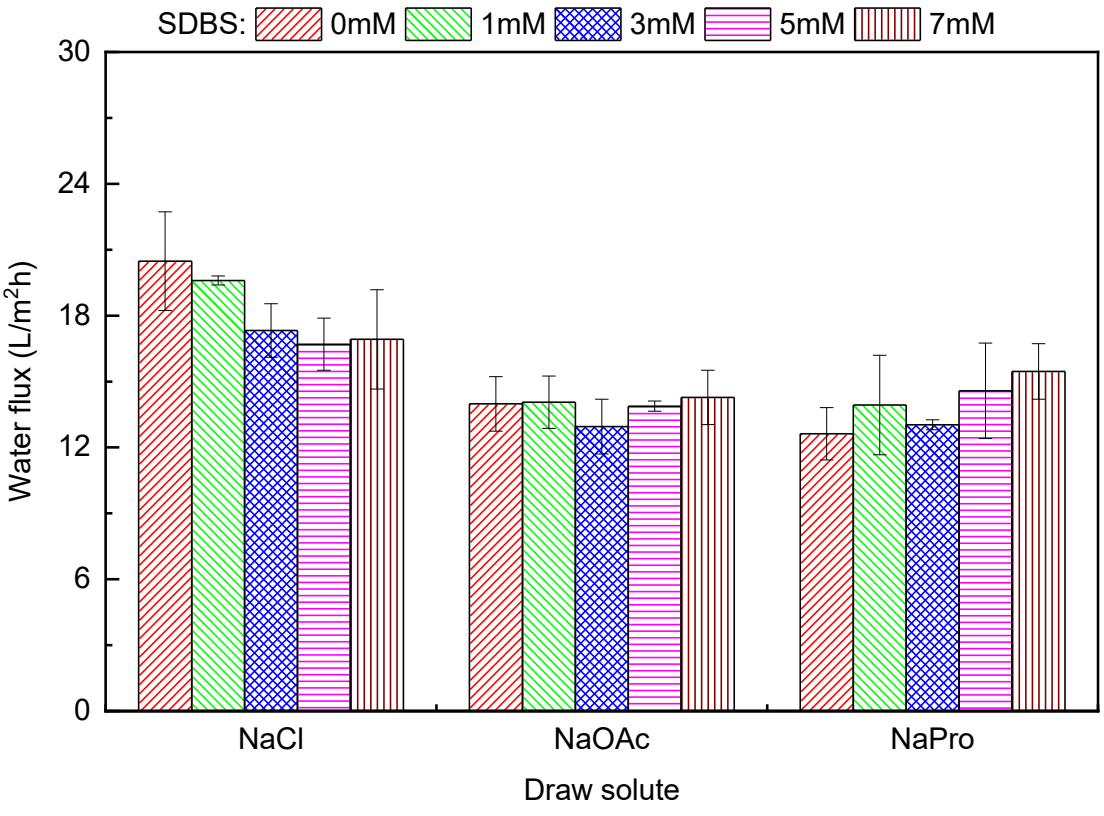


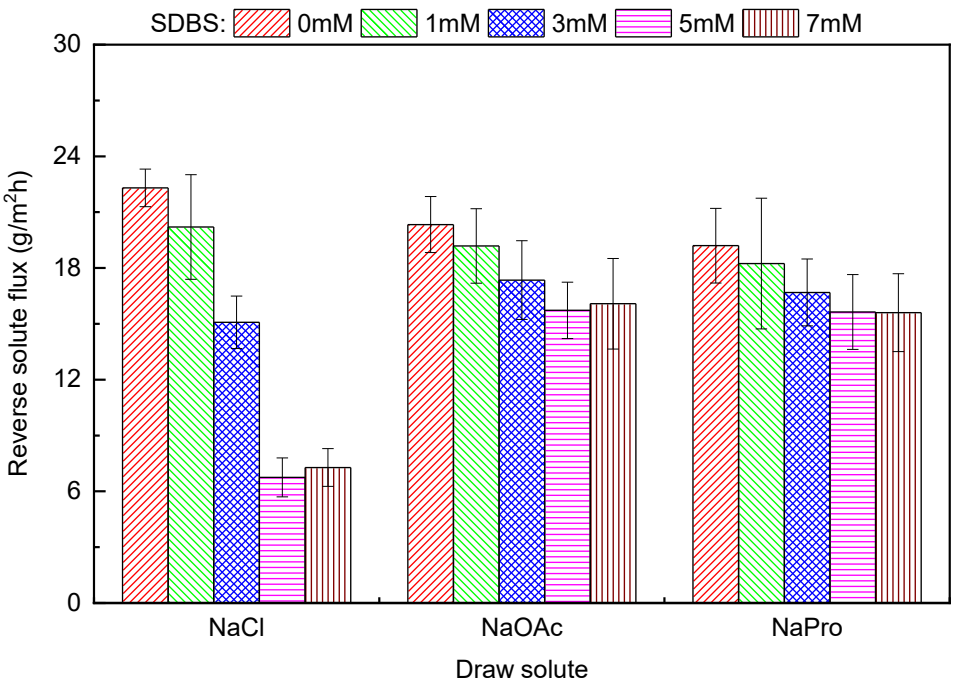
Fig. 1: Effects of different draw solutions with SDBS addition on FO water flux. FO was operated in osmotic dilution mode with deionized water feed and draw solutions at the same osmotic pressure of 60 bar. Cross-flow velocity of feed and draw solutions

was 8.3 cm/s. Error bars represent standard deviation from duplicate tests in a temperature-controlled room (25 ± 0.1 °C).

A comparable water flux was observed for NaOAc and NaPro draw solutions in response to SDBS addition. Unlike NaCl, increasing SDBS concentration in these two ionic organic draw solutions insignificantly affected the FO water flux. Only slight increase in the water flux was observed for NaPro. This result was due to the possibility that the enhanced hydrophilicity on the membrane supporting layer was more significant than the increased solution viscosity as NaPro has large molecular weight and thus resisted to interact with SDBS [39].

3.1.2 Reverse solute flux

SDBS addition could effectively reduce the reverse flux of all draw solutes (Fig. 2). Nevertheless, such reduction was only notable (approximately 69.7%) when SDBS concentration was lower than 5 mM. The reduced reverse solute flux could be attributed to micelle aggregation to narrow membrane pore size and/or to form a thin surfactant layer on the membrane supporting layer to block solute passage [27]. Moreover, SDBS had negatively charged heads and thus could effectively aggregate sodium ions via electrostatic attraction to enlarge the molecular size of draw solutes and reduce their diffusivity [20, 36]. Compared to the two ionic organic draw solutes, the reduction in reverse solute flux was more notable for NaCl due to its smaller molecular weight and thus high ion diffusion, which could be easily captured by SDBS for micelle aggregation [20, 40].



328

329 **Fig. 2:** Effects of SDBS addition on reverse flux of different draw solutes in FO
330 operation. Experimental conditions are shown in the caption of Fig. 1.

331 Specific reverse solute flux (SRSF) was calculated to comprehensively evaluate the
332 effects of SDBS addition on water and reverse solute fluxes (Fig. 3). All draw solutes
333 experienced a significant decline in SRSF, particularly with SDBS concentration up to
334 5 mM. Such reduction was more notable for NaCl in comparison to the two ionic
335 organic draw solutes due to its much higher water flux (Fig. 1) and lower reverse
336 diffusion (Fig. 2) in response to increased SDBS concentration. This result indicates
337 that the NaCl draw solute is more promising than its ionic organic counterparts for
338 OMBR operation with SDBS addition to alleviate reverse solute flux.

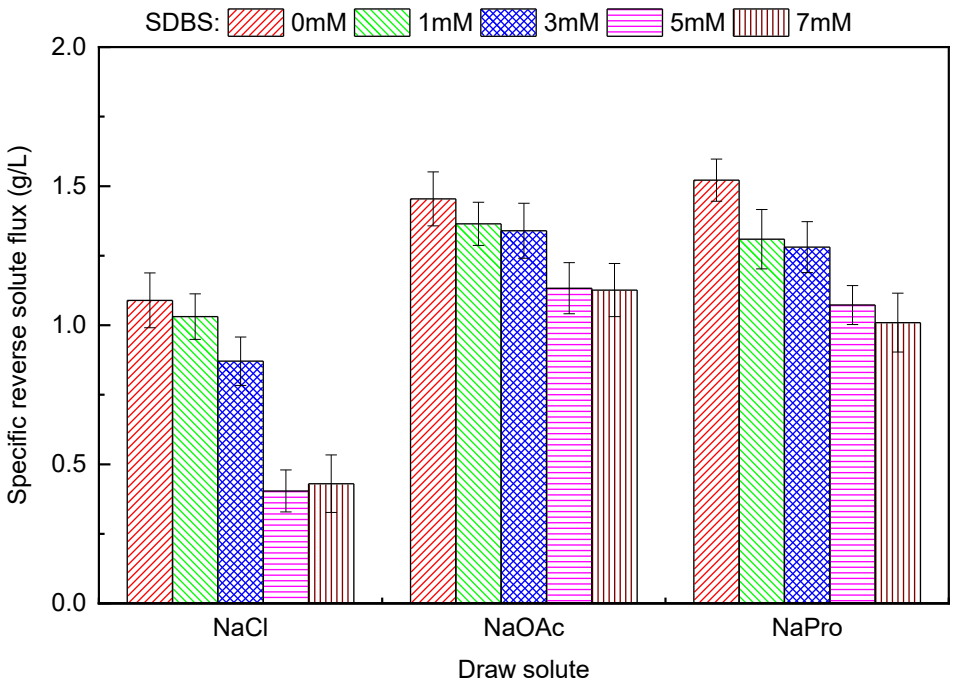


Fig. 3: Effects of SDBS addition on specific reverse solute flux of different draw solutes in FO operation. Experimental conditions are shown in the caption of Fig. 1.

3.2 Effects of SDBS addition on OMBR performance

Results reported above show that NaCl was more sensitive to SDBS addition than the two ionic organic draw solutes in FO operation. In particular, SDBS concentration up to 5 mM contributed to the lowest SRSF for NaCl with notable mitigation on reverse solute flux but insignificant hindrance on water permeation. Thus, two OMBR systems were compared in parallel to evaluate surfactant impacts using NaCl draw solution with and without 5 mM SDBS, respectively.

3.2.1 Salinity build-up and water production

Both OMBR systems experienced a continuous increase in salinity build-up in the bioreactor (indicated by the mixed liquor conductivity) (Fig. 4A). Such an increase could be attributed to the high salt rejection from wastewater by FO membrane and the reverse draw solute diffusion [9]. Compared to pure NaCl draw solution, SDBS addition could mitigate salinity build-up in the bioreactor, which was mainly related to the reduced reverse solute flux as discussed in section 3.1.2.

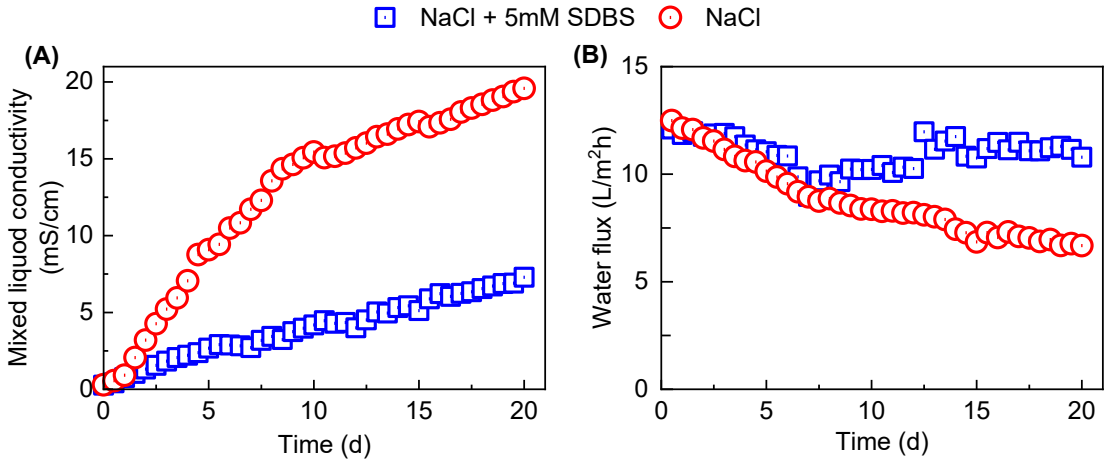


Fig. 4: (A) Mixed liquor conductivity and (B) water flux during OMBR operation with and without SDBS addition, respectively. Experimental conditions: draw solution = 1.2 M NaCl, 1.2 M NaCl + 5 mM SDBS surfactant; cross-flow velocity = 8.3 cm/s; DO = 4 mg/L; initial MLSS = 5 g/L; SRT = 20 d; temperature = 25 ± 1 °C; HRT was determined by the FO water flux.

A decrease in water flux was observed for the two OMBR systems (Fig. 4B). Since the draw solution was replaced every 12 hours, the observed flux decrease was mainly ascribed to salinity build-up in the bioreactor and membrane fouling [41]. The elevated salinity in the bioreactor could enhance osmotic pressure in the mixed liquor side, thereby reducing the net driving force (i.e. transmembrane osmotic pressure) for water permeation [18]. Moreover, a patchy and thin fouling layer was observed on the membrane surface at the conclusion of OMBR operation regardless of SDBS addition (Fig. S2, Supplementary Data).

Compared to pure NaCl draw solution, SDBS addition slightly reduced the OMBR water flux within the first 3 days (Fig. 4B). This result is consistent with that observed in FO tests due to the increased viscosity of the draw solution with SDBS addition to reduce the transmembrane osmotic pressure for water transport. Nevertheless, SDBS addition to the draw solution could effectively control salinity build-up in the bioreactor and thus sustain the OMBR water flux (approximately 10 L/m^{2}h) thereafter.

3.2.2 Biomass characteristics

SDBS addition to draw solution significantly improved biomass characteristics during OMBR operation (Fig. 5). It has been reported that the elevated bioreactor salinity could result in the dehydration and plasmolysis of microbial cells and thus inhibit sludge growth and activity in OMBR operation [16]. Thus, the MLVSS/MLSS ratio and sludge SOUR reduced in OMBR without SDBS addition (Fig. 5 A&B). Nevertheless, such reduction became negligible from day 15 onward, possibly due to microbial adaptation to the increased salinity [42]. Furthermore, microbial response to salinity build-up in the bioreactor enhanced both EPS and SMP concentrations in the mixed liquor (Fig. 5 C&D) through cell lysis and cellular secretion [43]. By contrast, adding SDBS to the draw solution alleviated salinity build-up in the bioreactor, thereby maintaining biomass characteristics during OMBR operation.

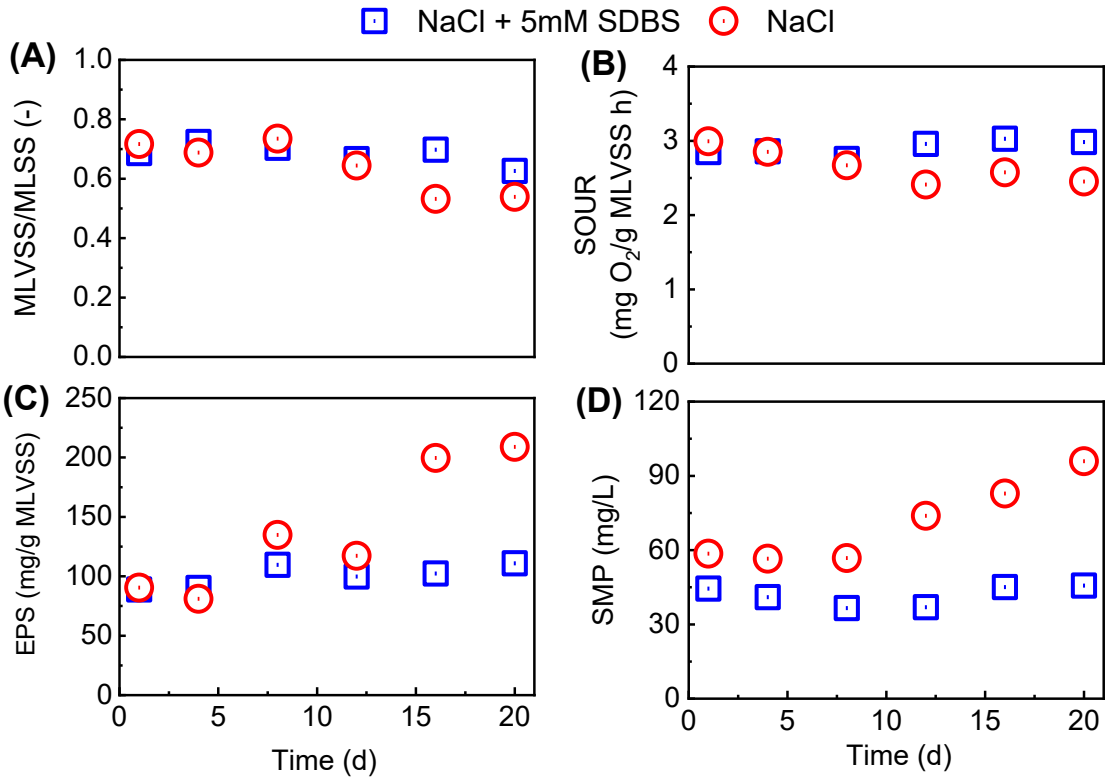


Fig. 5: Key biomass characteristics during OMBR operation with and without SDBS addition to the draw solution, respectively. Experimental conditions are shown in the caption of Fig. 4.

3.2.3 Removal of bulk organic matter and nutrients

By integrating biological treatment with highly selective aquaporin FO membrane,

OMBR could effectively remove both organic matter and nutrients in wastewater (Fig. 6&7). Nevertheless, salinity build-up in the bioreactor could negatively affect the biological treatment of OMBR. Of the two OMBR systems, TOC and NH_4^+ concentrations in the bioreactor increased from day 9 onward when no SDBS was added to the draw solution (Fig. 6). This observation consolidates the inhibitory effect of high salinity on the microbial metabolism, particularly susceptible nitrifiers in the mixed liquor [8]. For instance, Luo et al. [6] observed a notable decrease in NH_4^+ removal (from almost 100% to 38%) by a conventional MBR when the bioreactor salinity increased to 6 g/L NaCl. Nevertheless, the aquaporin FO membrane safeguarded over 98% TOC and 85% NH_4^+ removals by OMBR regardless of fluctuation in biological treatment. On the other hand, SDBS addition in the draw solution led to ignorable TOC and NH_4^+ concentrations in the bioreactor, indicating stable biological treatment over OMBR operation. It is noteworthy that TOC removal by OMBR with SDBS was not calculated since its addition increased organic content in the draw solution. In practice, an additional desalination process, such as RO and MD (using superhydrophobic or omniphobic membranes) can be potentially used to regenerate the draw solution with SDBS and produce recycling water.

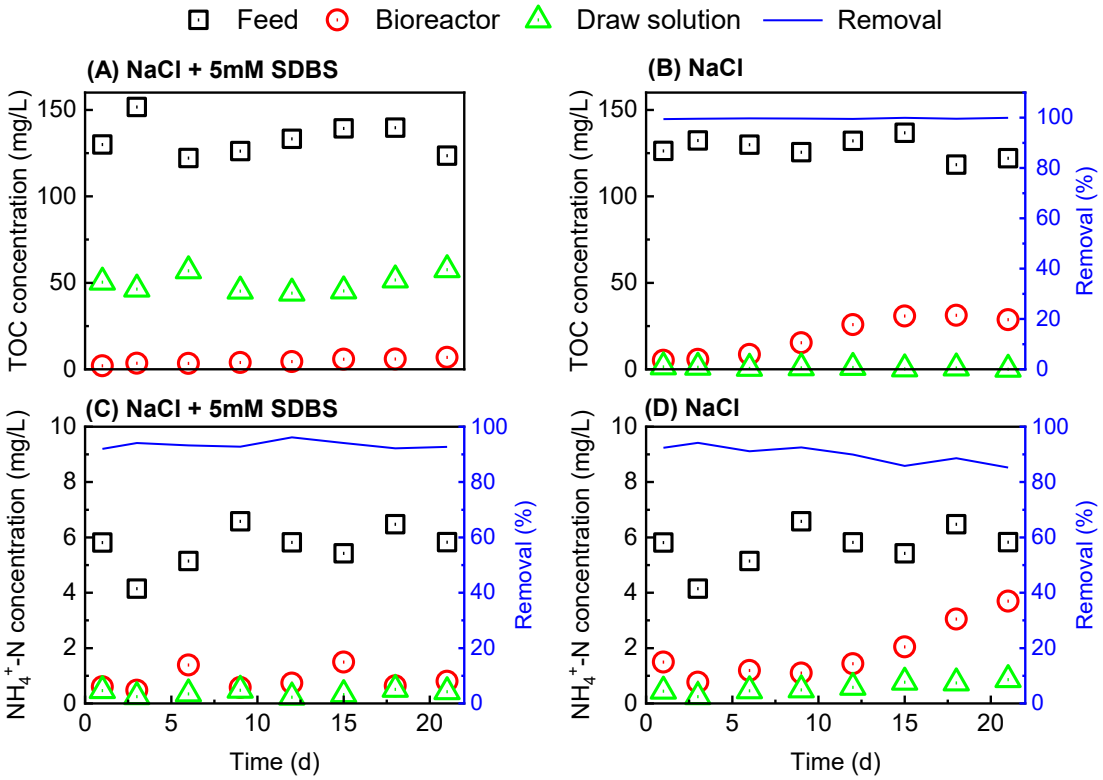


Fig. 6: (A & B) TOC and (C & D) NH_4^+ concentrations as well as their overall removal in OMBR operation with and without SDBS addition in the draw solution, respectively. Experimental conditions are shown in the caption of Fig. 4.

TN and TP cannot be effectively removed in activated sludge treatment as they largely rely on microbial assimilation [44]. Without denitrification, TN presents mainly in the form of NH_4^+, nitrite (NO_2^-), and nitrate (NO_3^-) in activated sludge. Since the aquaporin FO membrane could moderately retain these nitrogen species (approximately 60%) [10], TN accumulated considerably in the mixed liquor for the two OMBR systems (Fig. 7A&B). Nevertheless, the passage of these nitrogen species through the FO membrane reduced the overall TN removal by OMBR. In particular, adding SDBS to the draw solution could sustain water flux to increase the wastewater loading, thereby enriching TN in the bioreactor to deteriorate OMBR removal performance (Fig. 4B). Similarly, SDBS addition resulted in more notable TP accumulation in the bioreactor in comparison with the pure NaCl draw solution (Fig. 7 C&D). Nevertheless, the effective steric hindrance and electrostatic repulsion between the FO membrane and phosphate ions resulted in above 90% TP removal by both OMBR systems [10].

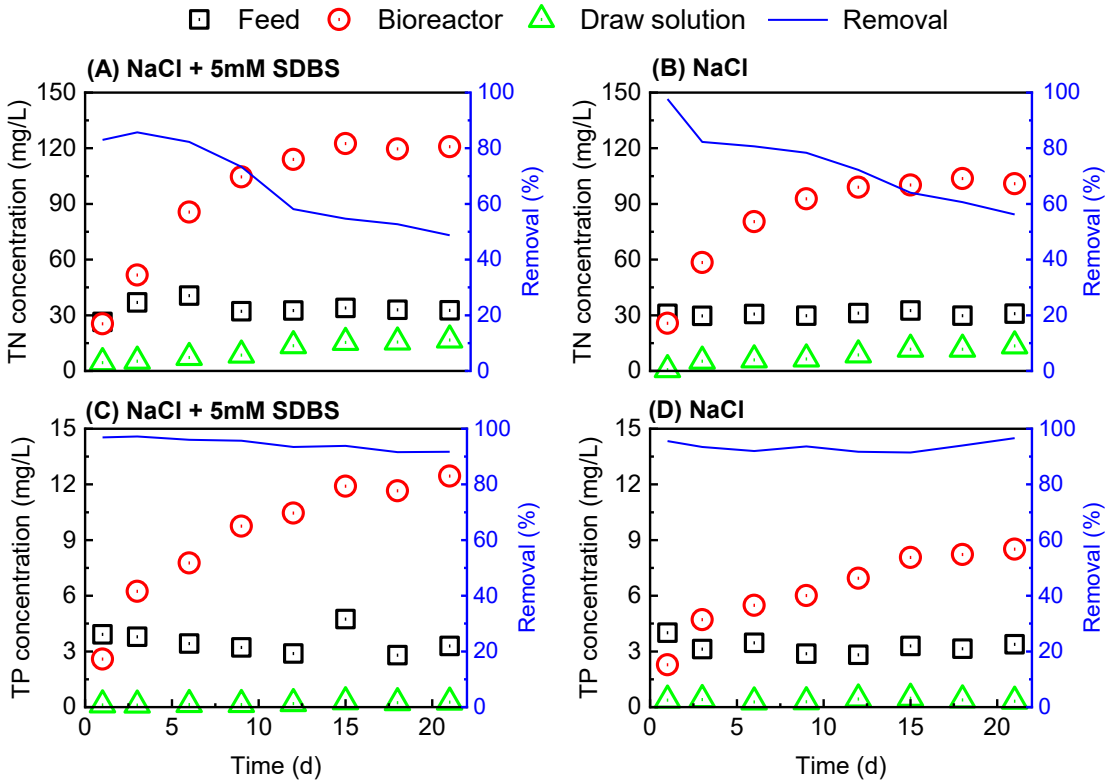


Fig. 7: (A and B) TN and (C and D) TP concentrations as well as their overall removal in OMBR operation with and without SDBS addition in the draw solution, respectively. Experimental conditions are shown in the caption of Fig. 4.

3.2.4 *Removal of pharmaceutically active compounds*

All 12 PhACs investigated in this study were removed by more than 90% in both OMBR systems (Fig. 8). Such effective removal could be ascribed to the complementarity between membrane retention and biological treatment. Indeed, Xie et al. [25] have demonstrated the high TrOC removal by the aquaporin FO membrane through steric hindrance and electrostatic interaction. Nevertheless, biological treatment, mainly including biodegradation, sludge adsorption, and/or biotransformation [45], was the dominant contributor to PhAC removal in OMBR.

Of the four PhAC groups categorized based on their attributes, the highest removal through biological treatment in OMBR was observed for sulfonamides, followed by tetracyclines, macrolides, and fluoroquinolones, respectively (Fig. 8). The effective removal of sulfonamides (90%) could be attributed to their high biodegradability by specific enzymes (e.g. ammonium monooxygenase) through microbial co-metabolism,

which has been considered as the main pathway for antibiotic biodegradation [45, 46]. Moreover, more than 80% removal was observed for both macrolides and tetracyclines from the two bioreactors. Given their high hydrophobicity (Log K_{ow} > 3), macrolides could readily adsorb onto activated sludge through hydrophobic interactions to facilitate biodegradation and/or biotransformation [47]. Although tetracyclines are relatively hydrophilic (Log K_{ow} < 0), they could be zwitterion in the mixed liquor with pH of approximately 7.5 and thus electrostatically attracted by activated sludge [45]. By contrast, fluoroquinolones have robust chemical structure and are recalcitrant to biodegradation. Thus, their removal in the two bioreactors only ranged from 59% to 74%, which could be largely attributed to sludge adsorption through electrostatic attraction [48].

Compared to the system without SDBS, a slightly higher removal of several PhACs (in the group of tetracyclines, macrolides, and fluoroquinolones) by biological treatment was observed for OMBR with surfactant (Fig. 8). This result is expected as SDBS addition mitigated salinity build-up in the bioreactor and thus maintained the biological stability. Indeed, recent studies have demonstrated that the elevated salinity could inhibit the activity of halophobic microorganisms, such as nitrifying bacteria that could biodegrade antibiotics through co-metabolism [6, 15, 49].

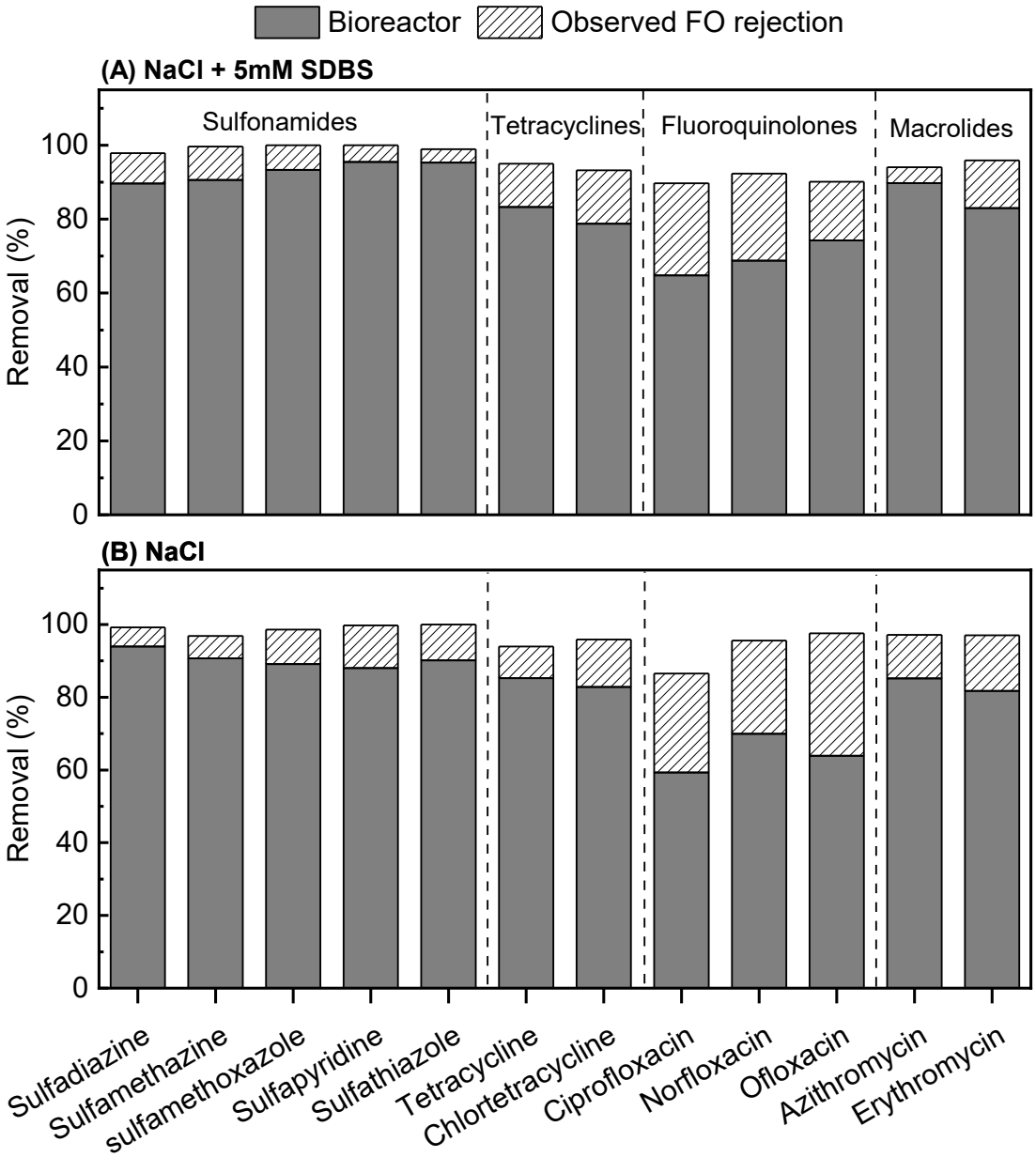


Fig. 8: Removal of PhACs by the biological treatment and the FO rejection during OMBR operation with and without SDBS addition to the draw solution, respectively. Average removal data obtained from three measurements (once every 7 days) were shown with the standard deviation in the range of 4% – 14%. The observed FO rejection showed the removal difference between the bioreactor and OMBR rather than its real retention capability. Experimental conditions are shown in the caption of Fig. 4.

4. Conclusion

Results reported here demonstrate that SDBS addition up to 5 mM could effectively reduce reverse draw solute flux with a slight decline in water flux during FO operation.

Such effect was more notable for NaCl draw solution in comparison to its two ionic organic counterparts (i.e. NaAOc and NaPro). Furthermore, adding SDBS to NaCl draw solution considerably mitigate salinity build-up in the bioreactor and thus sustain the water flux in OMBR operation. As a result, sludge characteristics and biological treatment were relatively stable in OMBR, contributing to effective biological removal of contaminants. Nevertheless, all 12 PhACs investigated could be highly removed by OMBR (> 90%) due to their effective retention by the FO membrane irrespective to SDBS addition to the draw solution.

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